

Plant Uptake of Selenium from Waste Sedimentary Rock Units and Their Potential Use as Capping Materials for Revegetated Waste Rock Dumps

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Background:

The phosphate rock mining industry removes soil and sedimentary rock units overlying phosphate rock ore units (Fig. 1) during the mining process and stores this soil and waste rock in stockpiles. Industry and land management agencies would like to use the waste rock as a capping material over seleniferous waste shale. The waste rock cap would be covered with stockpiled soils that would then be revegetated. A waste rock dump with a revegetated soil and waste rock cap over seleniferous shale is constructed to minimize plant uptake of Se and thus protect grazing animals from exposure to potentially toxic levels of Se in the waste shale.

Meade Peak Phosphatic Shale Cross-Section

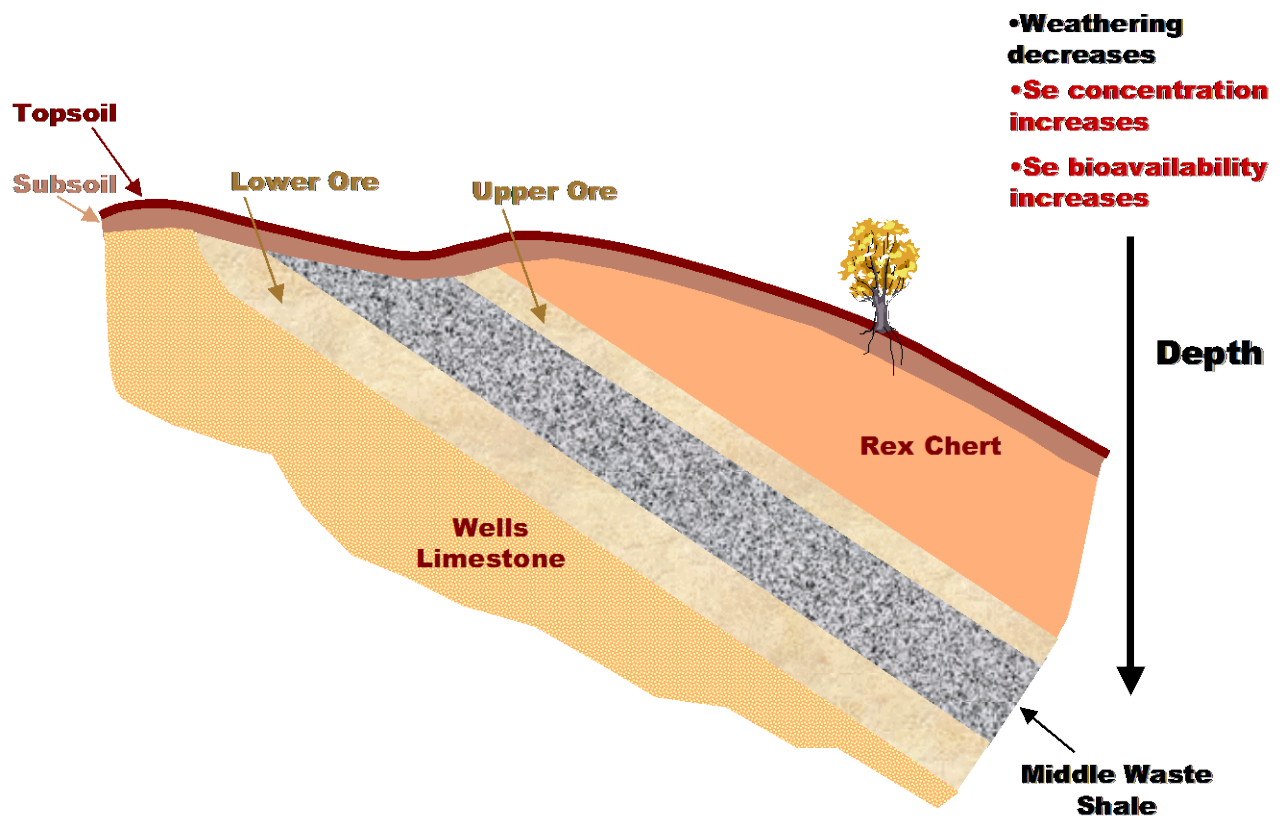


Fig. 1. Cross-section diagram of sedimentary rock units and expected changes in extent of physical and chemical weathering and Se concentrations and bioavailability with depth.

Phosphatic shales are enriched in Se and other trace elements. In general, Se concentrations in phosphatic shale decrease with increasing degree of alteration (i.e., weathering) of the shale (Herring and Grauch 2004). A significant fraction of the Se in phosphatic shale is water soluble (Herring 2004) and is available for plant uptake (Mackowiak et al. 2004). Perkins and Foster (2004) found that most of the Se in unweathered rocks of the Meade Peak Member of the Permian Phosphoria Formation is associated with the sulfide fraction with lesser amounts in organic matter and oxyhydroxide fractions and as elemental Se. In contrast, most of the Se in weathered rocks is found in the oxide fraction with lesser amounts in the organic matter fraction and as elemental Se. Thus, as mineral sulfide weathering progresses, Se is released and re-incorporated into the weathered metal oxide fractions. Although, the bioavailability of Se in each of its solid phase forms in phosphatic shale is largely unknown, some Se released during metal sulfide weathering is available for plant uptake.

The high degree of Se availability for plant uptake from phosphatic shale + soil mixtures led Mackowiak and Amacher (2005) to recommend that phosphatic shales that come into contact with plant roots on re-vegetated waste rock dumps should contain no more than 1 mg/kg total Se to keep plant Se concentrations below the 5 mg/kg recommended limit for forages (Food and Nutrition Board 1980).

Mackowiak and Amacher (2005) also evaluated Se uptake by plants growing in unmined Phosphoria Formation soils and found that, in general, such soils could be used as soil caps over seleniferous waste rock dumps. Their recommended Se levels for Phosphoria Formation soils used as revegetated waste rock dump caps were:

- < 13 mg/kg total Se in disturbed Phosphoria Formation soils (Test soils higher than this for plant uptake).
- < 50 mg/kg total Se in undisturbed Phosphoria Formation soils
- < 1.5 mg/kg oxalate-extractable Se.

The large volumes of waste sedimentary rock units such as Rex chert and Grandeur dolostone produced during phosphate ore mining may also have utility as waste rock dump caps as a sandwich layer overlying the seleniferous waste shale and underneath the vegetated soil cap. Some data on the Se content of these waste sedimentary rock units are available (e.g., Hein et al. 2004, Herring and Grauch 2004), but Se availability to plant uptake in these rock types is unknown.

Objectives:

- To determine plant uptake of Se from topsoil, chert, limestone and phosphatic shale.
- To determine relationships, if any, between plant Se concentrations and extractable and total soil Se levels in topsoil, chert, limestone, and phosphatic shale.
- To determine the effectiveness of different topsoil, chert, and limestone capping depth combinations at limiting plant uptake of Se from phosphatic shale.

- To classify chert and limestone units for suitability as waste rock dump capping materials using the USGS database of total Se levels in chert and limestone and results of glasshouse Se uptake experiments.

Methods:

Plant uptake of Se from topsoil, chert, limestone, and shale:

Bulk samples of topsoil, chert, limestone, and shale were supplied by Agrium. These materials were representative of the types of waste rock from the mining areas from which they were collected, but are not necessarily representative of waste rock from other areas. Three kilograms of each air-dried at ambient temperature and screened (<0.25-in) material were weighed into each of 4 replicate pots arranged in a randomized complete block experimental design. After uniform wetting from the bottom, each pot was fertilized with an $\text{NH}_4\text{NO}_3 + \text{KH}_2\text{PO}_4 + \text{KCl} + \text{MgSO}_4 + \text{FeEDTA}$ nutrient solution to supply 100 mg/kg N, 50 mg/kg P_2O_5 , 100 mg/kg K, 10 mg/kg Mg, 13 mg/kg S, and 0.6 mg/kg Fe. The pots were seeded with 50 alfalfa (*Medicago sativa* (MESA)) seeds between 0.25-in layers of pre-moistened germinating mix. The germinating mix was kept moistened until plants emerged and plants were watered as needed throughout the course of the experiment. Natural daylight was supplemented with 1000 W high-pressure sodium lamps to extend daylength to 15 hours and greenhouse temperature and humidity levels were monitored throughout the experiment. Plant topgrowth was harvested 46, 77, 103, and 147 days after planting and pots were re-fertilized with the nutrient solution after the first three harvests.

Effect of topsoil, chert, and limestone cap depths on plant uptake of Se from phosphatic shale:

The effectiveness of various depth combinations of topsoil, chert, and limestone caps for limiting plant uptake of Se from phosphatic shale was tested in a glasshouse experiment using large (30-cm diameter) PVC columns (Fig. 2). Three replicate columns of each of three column lengths were used (75, 150, and 210 cm). Capping materials, capping depths, and layer bulk densities for each column are summarized in table 1.

Each PVC column was housed in a metal cage structure for support and included a PVC drain at the bottom of the column. Sand and gravel layers (4-cm each) were placed at the bottom of each column. Columns were filled by slowly adding each capping material layer to achieve uniform distribution and settling of material. The topsoil, chert, limestone, and shale were not screened prior to filling the columns. Echo water content sensors connected to a Campbell Scientific datalogger were placed at 30-cm intervals in the columns as they were filled. To insure good contact between the water content sensor and capping material, the fine fraction (<2-mm) of each layer was packed around each sensor.

Table 1. Column lengths, capping material layer depths, and layer bulk densities.

Column	Column Length	Total Cap Depth	Topsoil		Chert		Limestone		Shale	
			Depth	ρ^1	Depth	ρ	Depth	ρ	Depth	ρ
	cm	cm	Cm	g/cm ³	cm	g/cm ³	Cm	g/cm ³	Cm	g/cm ³
1	75	15	15	0.94					52	1.47
2	75	15	15	1.12					52	1.32
3	75	15	15	1.08					52	1.42
4	150	90	30	0.95	30	1.57	30	1.46	52	1.34
5	150	90	30	0.90	30	1.63	30	1.61	52	1.38
6	150	90	30	0.88	30	1.54	30	1.58	52	1.38
7	210	150	30	0.86	60	1.53	60	1.37	52	1.47
8	210	150	30	0.90	60	1.54	60	1.33	52	1.49
9	210	150	30	0.78	60	1.58	60	1.47	52	1.37

¹ ρ = bulk density

Deionized water was added to each column at an application rate of 4 L/hr using a peristaltic pump to achieve uniform column wetting. Volumes of water added and drainage collected for each column are summarized in table 2. Volumes added were selected to thoroughly wet the columns and to produce approximately the same volume of drainage from each column. Drainage waters were saved for total dissolved Se analysis by HG-AAS.

Each column was seeded with 100 seeds of western wheatgrass (*Agropyron smithii* (AGSM)) sandwiched between pre-moistened layers of germinating mix. The germinating mix was kept moistened until plants emerged and plants were watered thereafter as needed throughout the course of the experiment. Volumes of water added were recorded and water content at each 30-cm depth interval in each column was monitored at 5 min intervals using the Echo water content sensors and datalogger.

Table 2. Initial volumes of water added and drainage collected for each column.

Column	Column Pore Volume	Volume added		Drainage collected	
		L	Pore volume	L	Pore volume
1	23	11.5	0.50	4.1	0.18
2	24	12.0	0.50	4.2	0.18
3	23	11.5	0.50	4.0	0.17
4	48	20	0.42	4.3	0.09
5	47	20	0.43	3.8	0.08
6	48	20	0.42	3.9	0.08
7	68	26	0.38	3.5	0.05
8	68	26	0.38	4.3	0.06
9	67	29	0.43	2.8	0.04

Approximately one-month after seeding, plants were fertilized with a solution of $\text{NH}_4\text{NO}_3 + \text{KH}_2\text{PO}_4 + \text{KCl}$ to supply 30 mg/kg of N, 10 mg/kg of P_2O_5 , and 30 mg/kg of K_2O to the top 15-cm of topsoil in each column. Plant topgrowth in each column was harvested 39, 67, 102, 305, 349, and 431 days after planting. Plants in columns 4 and 5 were not harvested at 349, and 431 days after seeding because of poor growth. Plants were re-fertilized after each harvest and about 1 month before the 4th harvest. The cutting and fertilizing schedule and fertilizer amounts are summarized in table 3.

Table 3. Cutting and fertilizing schedule and fertilizer amounts.

Date	Days after planting	Cutting	Column	N mg/kg ¹	P_2O_5 mg/kg	K_2O mg/kg
06/30/03	0	Seeding				
07/27/03	27		1-9	30	10	30
08/08/03	39	1	1-9	30	10	30
09/05/03	67	2	1-9	40	20	40
10/10/03	102	3				
10/13/03	105		1-9	40	20	40
03/24/04	268		1-3	100	50	100
03/24/04	268		4-9	200	100	200
04/30/04	305	4	1-3	100	50	100
04/30/04	305	4	4-9	200	100	200
06/13/04	349	5 ²				
06/23/04	359		1-3	100	50	100
06/23/04	359		6-9	200	100	200
09/03/04	431	6 ²				
09/10/04	438		1-3, 6-9	200	100	200

¹in top 15-cm of soil

²Columns 4 and 5 not harvested

Column Capping Study

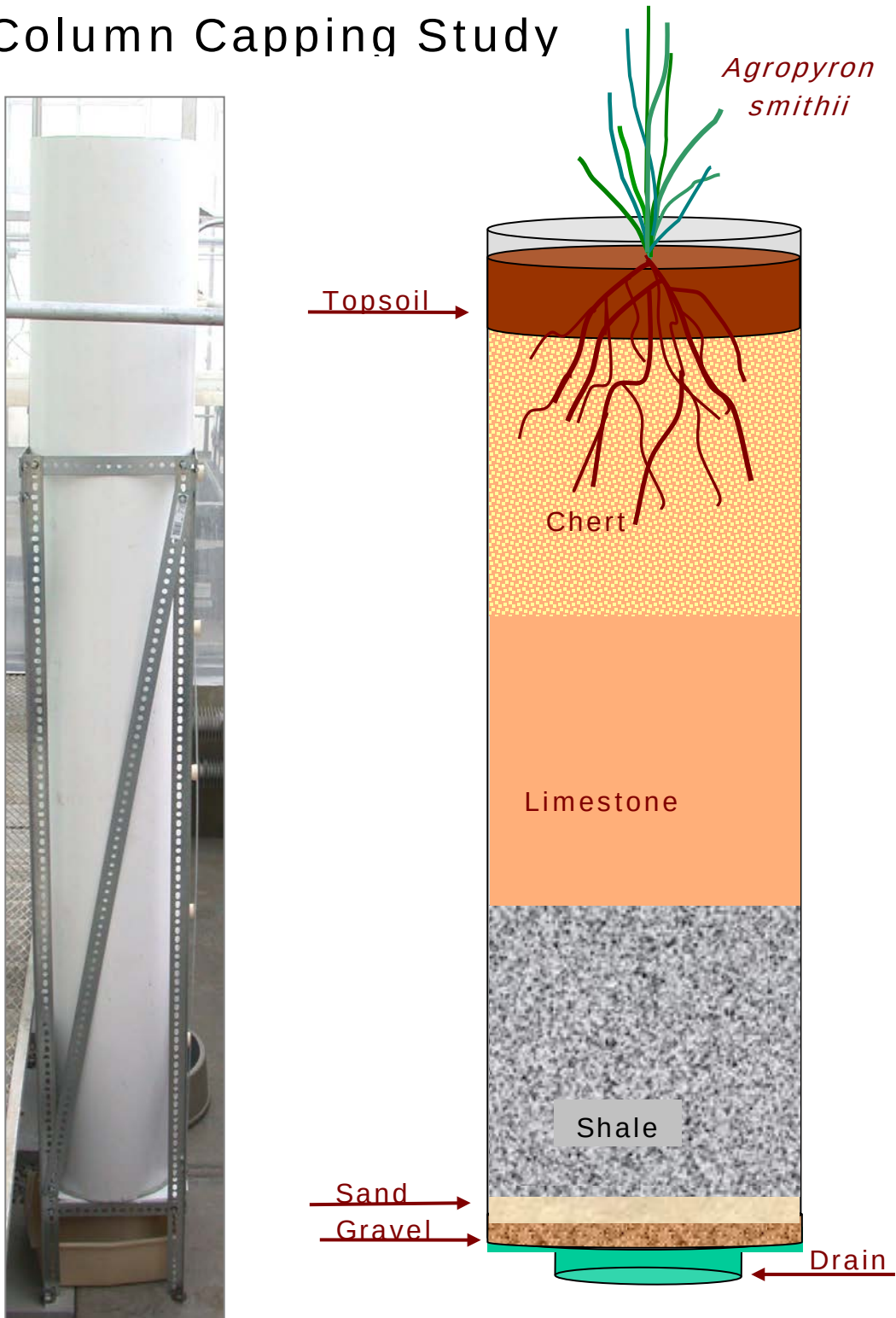


Fig. 2. Photo of 210-cm column (left) and cross-section of column with topsoil, limestone, and chert caps over waste shale (right).

Plant sample preparation and analysis:

Plant samples were dried in mechanical convection ovens at 60 C for 48 h, weighed, and ground to <20-mesh in a Willey mill before digestion. The $\text{HNO}_3 + \text{H}_2\text{O}_2$ digestion method of Jones (1989) was used to digest plant samples prior to analysis. Selenium in the digests was determined by hydride atomic absorption spectrophotometry (HG-AAS). To convert oxidized Se in the digests to Se(IV) for hydride analysis, equal volumes of digest and concentrated HCl were heated for 20 min at 80 C in a graphite block digester. Conversion efficiency was monitored by carrying a Se(VI) standard through the procedure. Also, several digest samples were spiked with known amounts of Se(IV) and Se(VI) and carried through the Se species conversion procedure. Reagent and method blanks, calibration standards, and check samples were also included as part of the lab QA/QC procedures.

Soil sample preparation and analysis:

Subsamples of the air-dried and screened (<0.25 in) topsoil, chert, limestone, and shale were further sieved through a <2-mm stainless steel sieve to remove coarse fragments and subsamples of the <2-mm material were rolled in glass scintillation vials with steel pins to pulverize the material to <100 mesh prior to digestion for total recoverable Se.

To determine total recoverable Se, 0.500-g subsamples of <100 mesh topsoil, chert, limestone, and shale were digested in 20 mL of a 3.5:1 mixture of concentrated $\text{HNO}_3 + \text{concentrated HClO}_4$ in glass digestion tubes in a graphite block digester at 95 C (Amacher et al. 2001, Amacher 2003). Digestion was complete when the volume was reduced to <2 mL and fumes of HClO_4 were visible. The digests were diluted to 50 mL with deionized water prior to analysis. To convert oxidized Se in the digests to Se(IV) for hydride analysis, equal volumes of digest and concentrated HCl + 1 mL of 0.1 M potassium persulfate were heated for 20 min at 80 C in a graphite block digester. Conversion efficiency was monitored by carrying a Se(VI) standard through the procedure. Also, several digest samples were spiked with known amounts of Se(IV) and Se(VI) and carried through the Se species conversion procedure. Digestion and analysis accuracy was verified by periodically analyzing three USGS sedimentary rock check samples collected, prepared, and analyzed for the Western US Phosphate Project (Herring and Wilson 2001).

Saturation extracts of <2-mm topsoil, chert, limestone, and shale were prepared as outlined by Rhoades (1996). The saturation extracts were analyzed for total dissolved Se by HG-AAS as before.

Phosphate-extractable Se was determined by shaking 2-g samples of <2-mm topsoil, chert, limestone, and shale with 40 mL of pH 7.2, 0.01 M $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ solution for 2 hr at 150 rpm, filtering the suspensions through quantitative filter paper, and analyzing the extracts for total dissolved Se by HG-AAS.

Oxalate-extractable Se was determined by shaking 0.500-g samples of <2-mm topsoil, chert, limestone, and shale with 25 mL of 0.2 M ammonium oxalate + 0.2 M oxalic acid for 2 hr at 150 rpm, filtering the suspensions through quantitative filter paper, and analyzing the extracts for total dissolved Se by HG-AAS.

Glasshouse experiment data analysis:

The effect of growth medium (topsoil, chert, limestone, and shale) and cap depth on Se uptake by AGSM was tested using the SAS (Statistical Analysis Systems, Cary, NC) mixed model with repeated measures (harvests).

Analysis of risk potential of increased Se uptake from chert and limestone caps based on the USGS database of Se levels in chert and limestone:

The USGS has compiled an extensive database of Se levels in various strata from the Rex chert, Meade Peak phosphatic shale, and Grandeur dolostone members of the Phosphoria Formation (Hein et al. 2004; Herring and Grauch 2004). We stratified these data by sedimentary rock unit and lithology and prepared box plots of the distribution of Se concentrations to determine which sedimentary rock units and lithologies had Se concentrations above or below recommended Se limits as determined from the glasshouse experiments. This type of analysis can help segregate and stockpile different sedimentary rock units and lithologies in the field into waste rock suitable for waste rock dump caps and waste rock that should be buried with phosphatic shale and not used as capping material.

Results and Discussion:Plant uptake of Se from topsoil, chert, limestone, and shale:

MESA biomass in topsoil increased from cutting 1 to cutting 2, but then declined in cuttings 3 and 4 (Fig. 3). MESA biomass in chert increased slightly from cuttings 1 through 4, whereas biomass in limestone did not change from cuttings 1 through 4 (Fig. 3). MESA biomass in phosphatic shale remained low for cuttings 1 and 2, but there was a relatively large increase for cuttings 3 and 4 (Fig. 3). We observed low initial growth rates of MESA in phosphatic shale in other experiments. Apparently, MESA grows poorly in 100 % phosphatic shale until it gets well established. This may be related to high concentrations of Zn and other trace elements in the shale that can inhibit plant growth. One or more harvests may be necessary to lower bioavailable levels of Zn in the shale via biomass removal. Despite some variation in MESA biomass among cuttings in some growth media, for all four cuttings, there were no statistically significant differences among mean MESA biomass attributable to growth media (table 4).

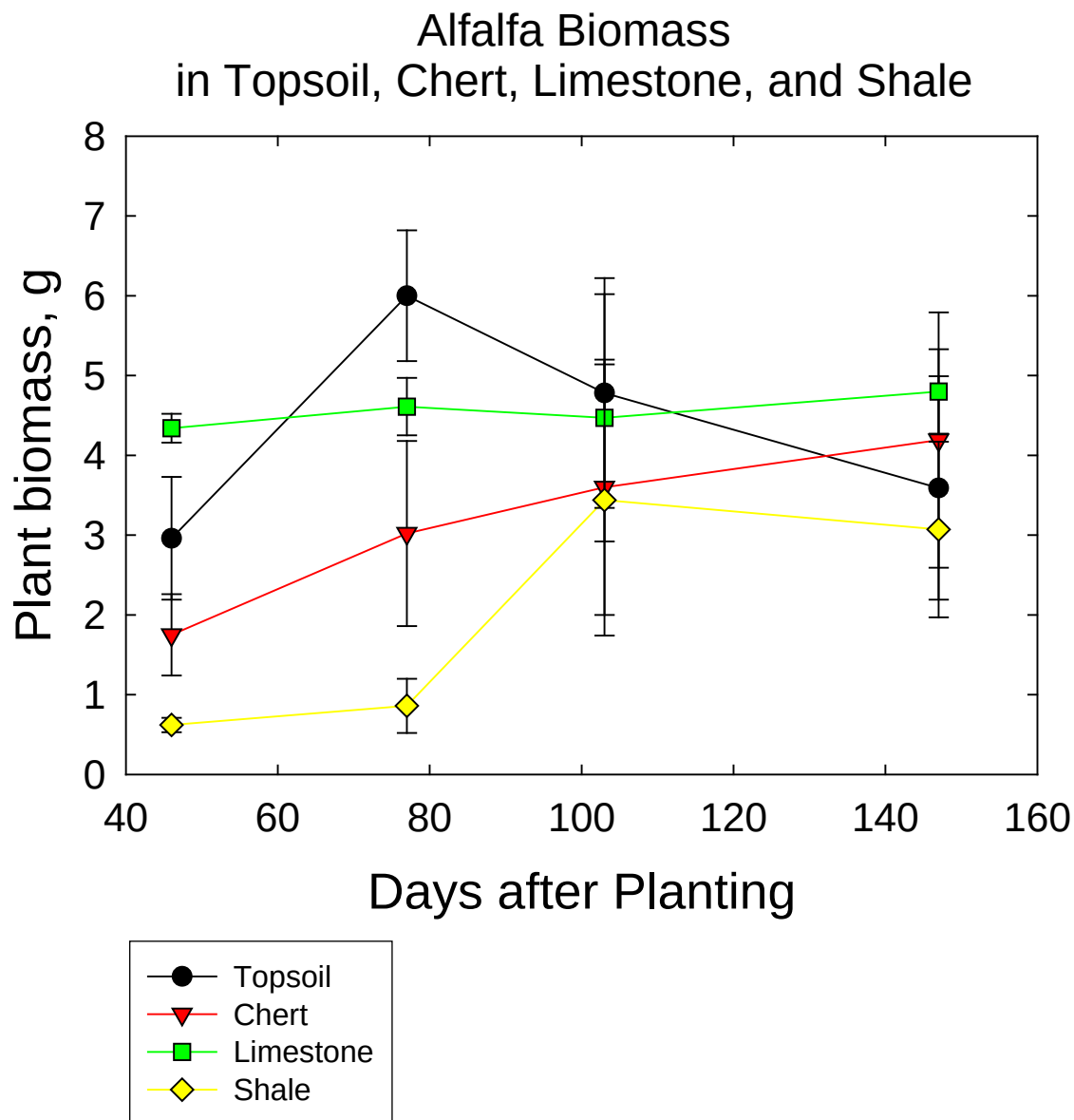


Fig. 3. Mean $\pm$ standard error MESA above-ground biomass in topsoil, chert, limestone, and shale at four cuttings.

Selenium concentrations in MESA grown in phosphatic shale, chert, and limestone all decreased from cutting 1 to cutting 4 (Fig. 4). The largest decrease was from cutting 1 to cutting 2 for MESA in phosphatic shale. Selenium concentrations in MESA in phosphatic shale did not change significantly from cuttings 2 through 4. There was a linear decrease in MESA Se in chert from cuttings 1 through 4, whereas MESA Se concentrations in limestone decreased only slightly over the course of the experiment. Selenium concentrations in MESA grown in topsoil increased in cuttings 1 through 3 and then decreased in cutting 4.

The order of Se uptake for the four growing media was phosphatic shale > chert > limestone > topsoil. For all four cuttings, differences in mean MESA Se among growth media were significantly different except between chert and limestone (table 4).

Only MESA grown in phosphatic shale exceeded the 5 mg/kg recommended limit for Se in forages (Fig. 4). Selenium concentrations in MESA grown in the topsoil, chert, and limestone capping materials remained well below 5 mg/kg for all four cuttings indicating that it is safe to use this soil and these sedimentary rock units as capping materials over seleniferous waste shale for plant community establishment.

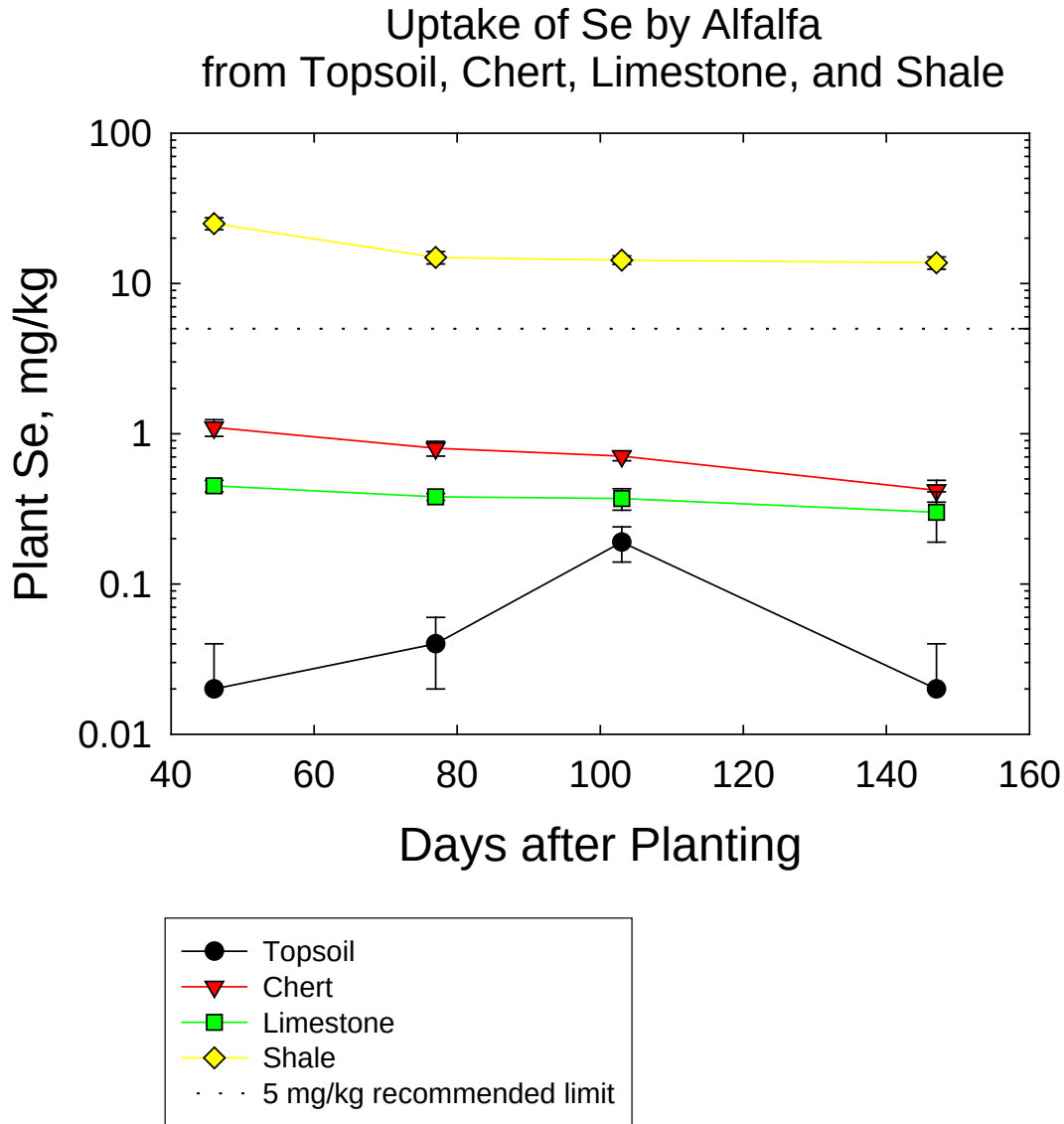


Fig. 4. Mean $\pm$ standard error Se concentrations in MESA grown in topsoil, chert, limestone, and shale at four cuttings.

Table 4. Mean $\pm$ standard error biomass and Se concentrations for four cuttings of MESA grown in topsoil, chert, limestone, and shale. Means not followed by the same letter are significantly different ($p < 0.01$).

Growth media	Mean biomass (4 cuttings)	Mean Se (4 cuttings)
	g	mg/kg
Topsoil	4.34 ± 0.50 a	0.03 ± 1.21 a
Chert	3.14 ± 0.50 a	0.70 ± 1.21 b
Limestone	4.56 ± 0.50 a	0.34 ± 1.21 b
Shale	2.00 ± 0.50 a	16.26 ± 1.21 c

Saturation extract, phosphate-extractable, oxalate-extractable, and total Se levels in the topsoil and sedimentary rock units (chert, limestone, and shale) are listed in table 5. Total Se in the topsoil and chert were very similar. Total Se in limestone and phosphatic shale were similar to each other and significantly higher than that in topsoil and chert. Saturation extract Se concentrations ranged from a low of 4 ug/L in topsoil to a high of 44 ug/L in shale. The order of saturation extract Se concentrations was shale > chert ~ limestone > topsoil. Phosphate extractable Se levels in chert and shale were similar and much higher than those found in limestone and shale. Oxalate-extractable Se in shale was much higher than that found in topsoil, chert, and limestone. Limestone had the lowest level of oxalate-extractable Se.

Table 5. Saturation extract, phosphate-extractable, oxalate-extractable, and total recoverable Se in topsoil, chert, limestone, and shale

Growth media	Saturation Extract Se	Phosphate-extractable Se	Oxalate-extractable Se	Total Recoverable Se
	mg/L	mg/kg	mg/kg	mg/kg
Topsoil	0.004 ± 0.001 ¹	0.023 ± 0.017	0.149 ± 0.048	5.45 ± 1.15
Chert	0.022 ± 0.001	0.075 ± 0.004	0.167 ± 0.038	5.20 ± 0.4
Limestone	0.018 ± 0.003	0.010 ± 0.002	0.045 ± 0.010	33.1 ± 2.8
Shale	0.044 ± 0.005	0.073 ± 0.001	3.851 ± 0.953	44.8 ± 8.9

¹mean $\pm$ standard error

The extractable Se results give some insight into bioavailable amounts of Se in these materials and help explain the plant uptake results. A strong linear relationship was found between plant uptake of Se in the different growth media and saturation extract Se concentrations (Fig.5 top). Jump and Sabey (1989) found that Se concentrations in soil saturation extracts gave the best correlation to plant uptake of Se compared to other Se soil tests they evaluated (hot water, DTPA, AB-DTPA, Na_2CO_3). Thus, saturation extracts, which measure water soluble Se, give the best measure of the most bioavailable fraction of Se in the soil or sedimentary rock material.

No relationship between plant uptake of Se and total Se was found (Fig. 5 bottom). The forms of Se in these materials differ greatly as indicated by the extraction

results (table 5) and plant uptake results (Fig. 4). Thus, total Se will not work as an indicator of plant available Se levels for comparing geological materials of greatly differing mineral composition and properties. However, within a given type of geological material (e.g., Phosphoria Formation soils), total Se is related to plant uptake once a threshold value is exceeded (Mackowiak and Amacher 2005).

Phosphate-extractable Se could not distinguish between chert and shale with respect to plant uptake of Se. Both materials had the same level of phosphate-extractable Se, but very different amounts of plant uptake of Se (Fig. 6 top).

Oxalate extractions, on the other hand, proved a good choice for discriminating among the various growth media for plant available Se. Limestone and shale had somewhat similar levels of total Se, but very different levels of oxalate-extractable Se that reflected plant uptake of Se from these materials (Fig. 6 bottom). Oxalate-extractable Se did not correlate with plant uptake of Se as well as saturation extracts because of the higher level of oxalate-extractable Se in topsoil than in limestone. This may reflect some unknown difference in properties between the two very different materials. Excluding the topsoil, there was an excellent linear relationship between plant uptake of Se and oxalate-extractable Se for limestone, chert, and shale. For sedimentary rock units, oxalate extractions show great promise for classifying these materials by Se bioavailability. Oxalate extractions are much faster and easier to carry out than the somewhat time-consuming saturation extracts.

Based on the results of this glasshouse experiment, we tentatively recommend the following limits for total Se in chert and limestone used as caps over seleniferous waste shale:

Chert: < 5 mg/kg total Se. Higher Se cherts might be safe to use as waste rock caps but should be tested for plant uptake before use.

Limestone: < 35 mg/kg total Se

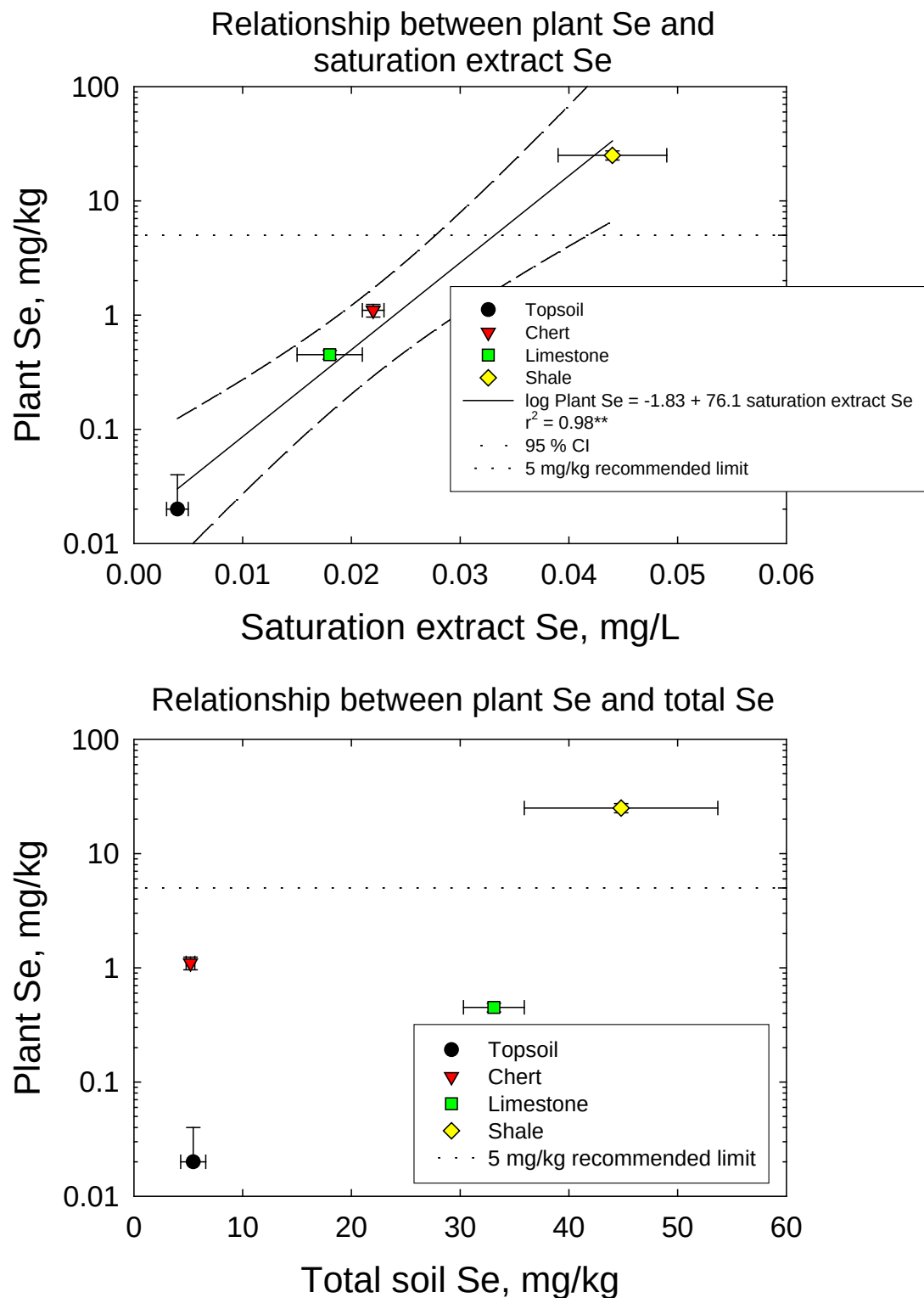


Fig. 5. Relationships between Se concentrations in MESA and growth media saturation extract (top) and total (bottom) Se.

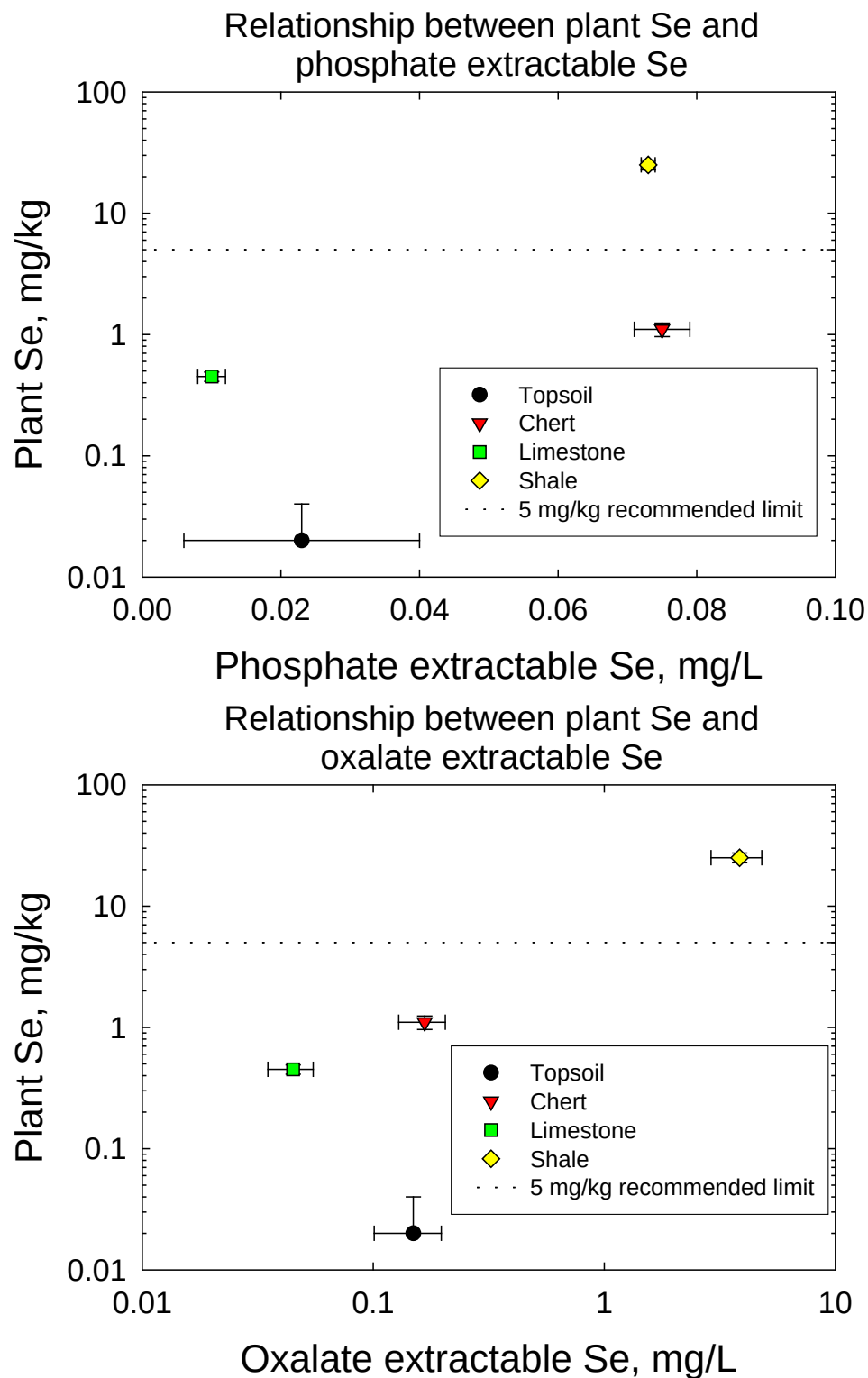


Fig. 6. Relationships between Se concentrations in MESA and phosphate-extractable and oxalate-extractable Se in growth media.

Effect of topsoil, chert, and limestone cap depths on plant uptake of Se from phosphatic shale:

Selenium concentrations in the drainage water from the columns after the initial water saturation ranged from 66 to 225 ug/L (table 6). Amounts of Se removed by the drainage water were calculated by multiplying the Se concentration in the drainage water by the volume of drainage collected (table 6). The Se removed in the column drainage water is the most water-soluble form of Se in the column and is no longer available for plant uptake, but this situation is no different than that found at waste rock dumps where snowmelt percolating through the dumps each year removes water-soluble Se, which appears in seeps at the base of the dumps and is no longer available for uptake by plants growing on the dumps. Concentrations of Se in the column initial drainage water were similar to those found in Wooley Valley unit 4 waste rock dump seeps (Stillings and Amacher 2004).

Table 6. Se concentrations in column drainage after initial saturation.

Column	Column Pore Volume	Volume added		Drainage collected		Se in drainage	
		L	Pore volume	L	Pore volume	ug/L	ug
1	23	11.5	0.50	4.1	0.18	90	369
2	24	12.0	0.50	4.2	0.18	66	277
3	23	11.5	0.50	4.0	0.17	90	360
4	48	20	0.42	4.3	0.09	125	538
5	47	20	0.43	3.8	0.08	103	391
6	48	20	0.42	3.9	0.08	70	273
7	68	26	0.38	3.5	0.05	183	640
8	68	26	0.38	4.3	0.06	116	499
9	67	29	0.43	2.8	0.04	225	630

Mean amounts of Se removed via drainage for the three cap depths are reported in table 7. Columns 1 through 3 had 15 cm of topsoil over 52 cm of phosphatic shale. Virtually all Se in the initial drainage water from columns 1-3 would have come from the shale because of the relatively high level of saturation extract Se in the shale compared to the topsoil (table 5). Adding 30 cm each of chert and limestone to columns 4-6 between the topsoil and shale layers did not significantly increase the amount of Se in the drainage water (table 7). Adding an additional 30 cm each of chert and limestone to columns 7-9 significantly increased the amount of Se in the drainage water but the increase was not large (table 7). Chert and limestone contribute only minor amounts of soluble Se to the overall capping system.

Table 7. Mean $\pm$ standard error amounts of Se in column drainage after initial saturation. Means not followed by the same letter are significantly different ($p < 0.01$).

Cap depth	Mean amount of Se in drainage water
cm	ug
15	335 $\pm$ 29 a
90	401 $\pm$ 77 ab
150	590 $\pm$ 45 b

Cap depth had no significant effect on AGSM biomass (Fig. 7, table 8), but there were significant differences among cuttings. AGSM above-ground biomass increased from cutting 1 (8/8/03) to cutting 2 (9/5/03) as the plants grew rapidly, but then declined by cutting 3 (10/10/03) as daylight decreased (Fig. 7). No supplemental lighting was used in this experiment. The plants remained largely dormant during the winter months. The 1st cutting in the 2nd growing season after seeding had about the same amount of biomass as the first three cuttings during the first growing season. Above-ground biomass remained below 30 g per column until cuttings 5 and 6 during the 2nd growing season when biomass increased in all columns. Columns 4 and 5 were not harvested at cuttings 5 and 6 because of poor growth, but column 6 had the most biomass of all columns in cuttings 5 and 6.

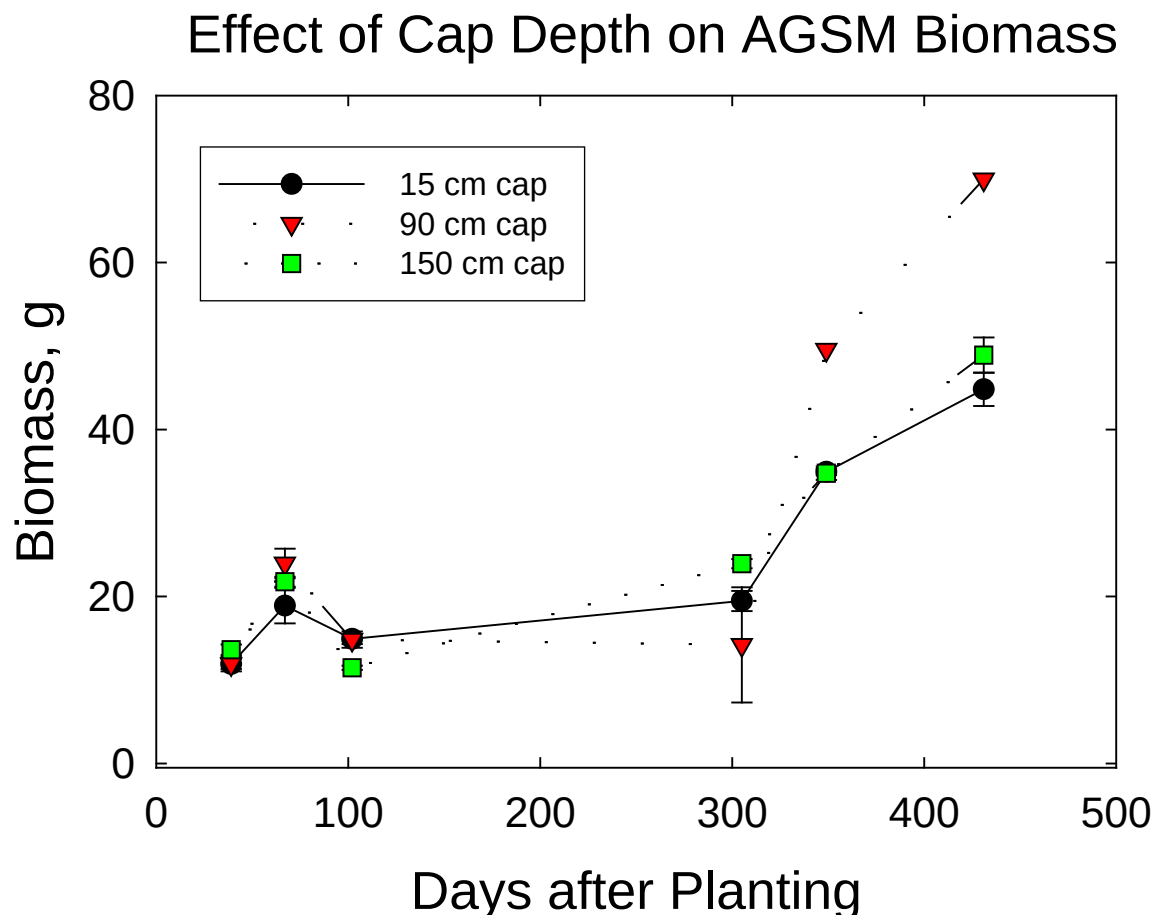


Fig. 7. Effect of cap depth over phosphatic shale (44.8 ± 8.9 mg/kg total Se) on mean $\pm$ standard error biomass of AGSM at six cuttings. 15-cm cap = 15 cm of topsoil, 90-cm cap = 30 cm of topsoil + 30 cm of chert + 30 cm of limestone, 150-cm cap = 30 cm topsoil + 60 cm of chert + 60 cm of limestone. Phosphatic shale depth = 52 cm.

Selenium levels in AGSM from the columns with the 90 and 150-cm caps were below those in AGSM from the columns with the 15-cm cap for cuttings 1 and 2 (Fig. 8). Plant roots were not fully developed at this point in the experiment so roots did not penetrate the capping layers to the phosphatic shale layer. By cutting 3, plant roots had penetrated the cap layers and were into the phosphatic shale layer and thus, Se concentrations in AGSM were not significantly different among the three cap depths. Capping depth did not influence above-ground plant Se levels during the 2nd growing season and Se concentrations remained at about the same level from cuttings 3 through 6. Mean AGSM Se for all six cuttings was not significantly influenced by cap depth (table 8).

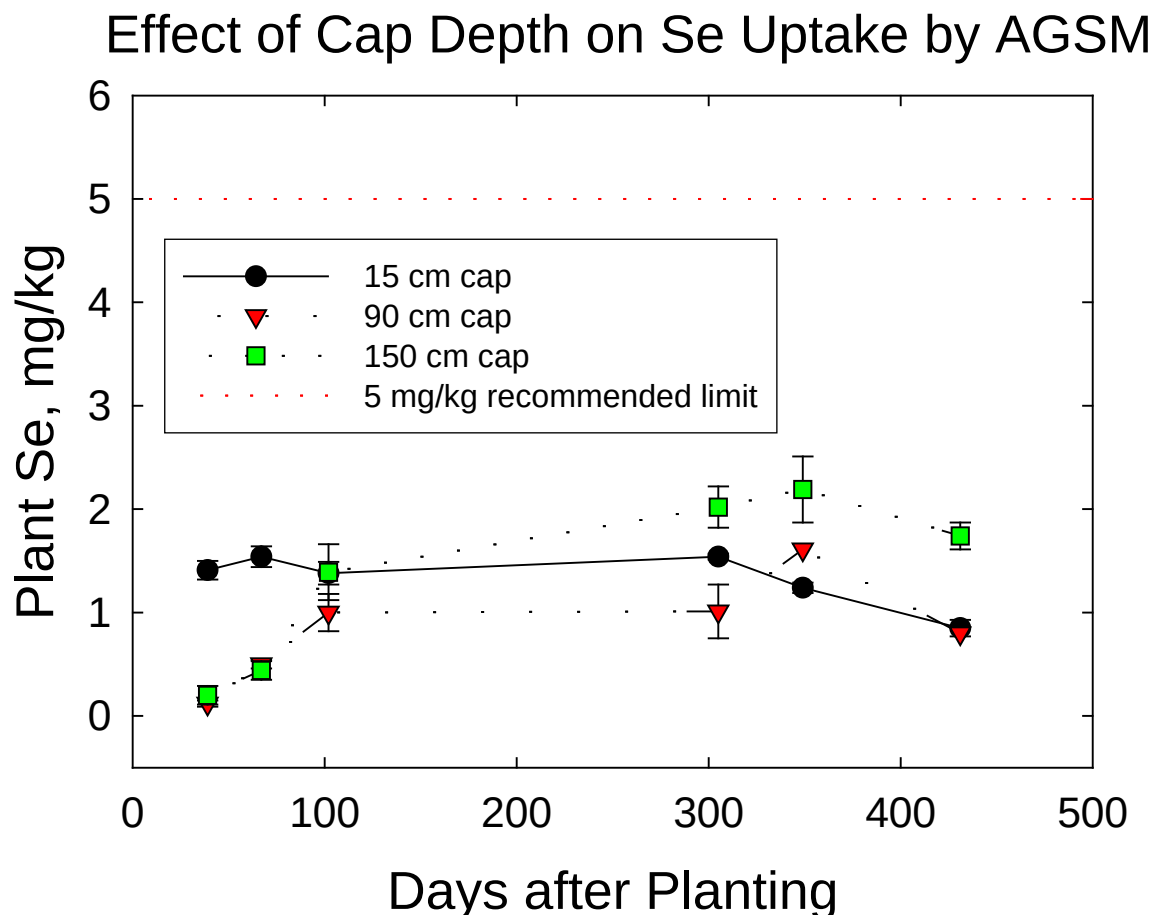


Fig. 8. Effect of cap depth over phosphatic shale (44.8 ± 8.9 mg/kg total Se) on mean $\pm$ standard error Se concentrations in AGSM at six cuttings. 15-cm cap = 15 cm of topsoil, 90-cm cap = 30 cm of topsoil + 30 cm of chert + 30 cm of limestone, 150-cm cap = 30 cm topsoil + 60 cm of chert + 60 cm of limestone. Phosphatic shale depth = 52 cm.

Table 8. Mean $\pm$ standard error biomass and Se concentrations for six cuttings of AGSM grown in columns with 15, 90, and 150 cm of capping material. Means not followed by the same letter are significantly different ($p < 0.01$).

Cap depth	Mean biomass (6 cuttings)	Mean Se (6 cuttings)
cm	g	mg/kg
15	24.2 ± 1.4 a	1.33 ± 0.11 a
90	28.3 ± 1.7 a	0.79 ± 0.12 a
150	25.8 ± 1.4 a	1.33 ± 0.11 a

No relationship between above-ground AGSM Se concentrations and biomass was found (Fig. 9), although the total amount of Se removed by harvesting above-ground plant growth generally increased during the 2nd growing season because of the increase in plant biomass in cuttings 5 and 6 (Fig. 10).

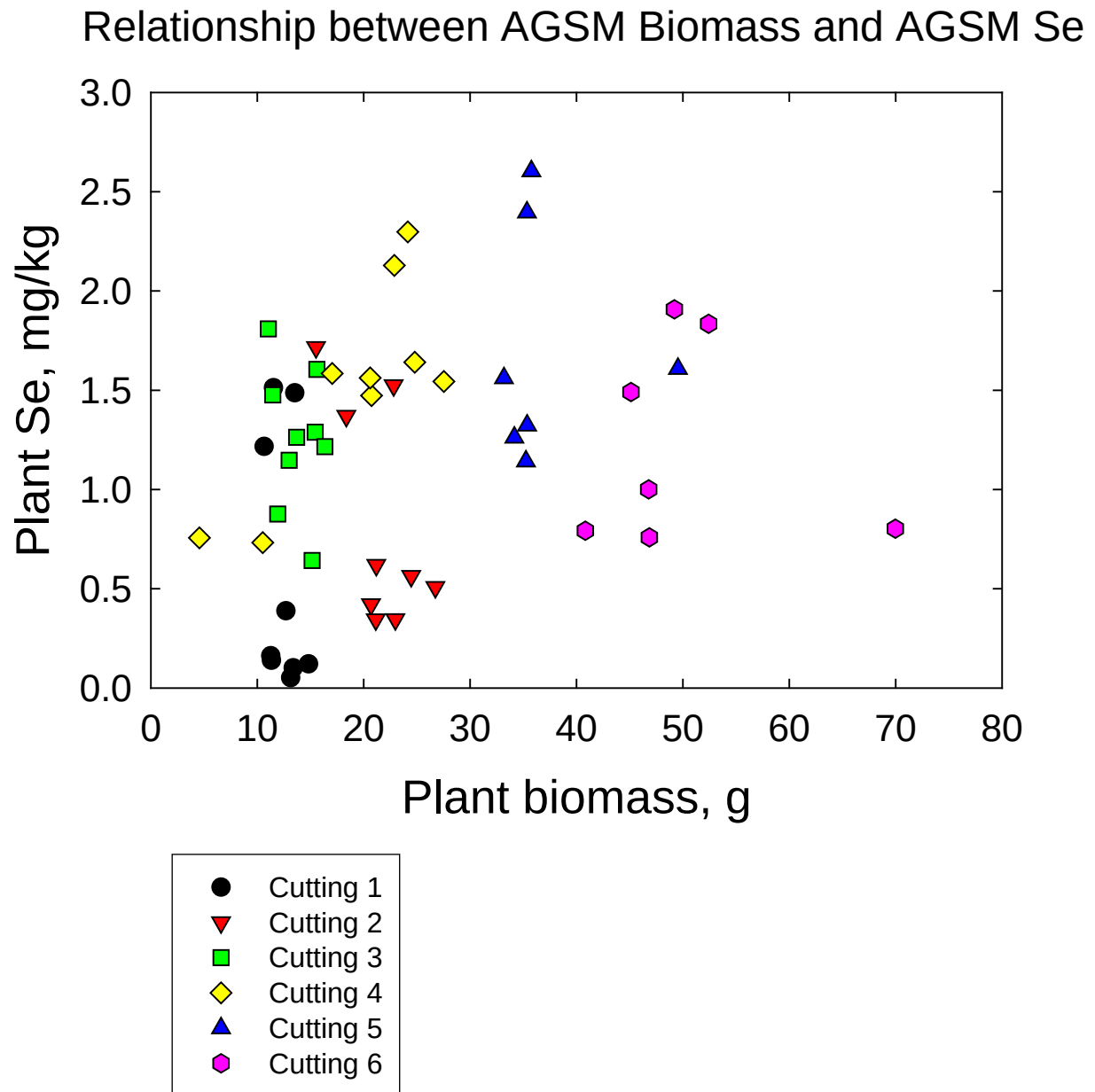


Fig. 9. Relationship between Se concentrations and biomass of AGSM at six cuttings.

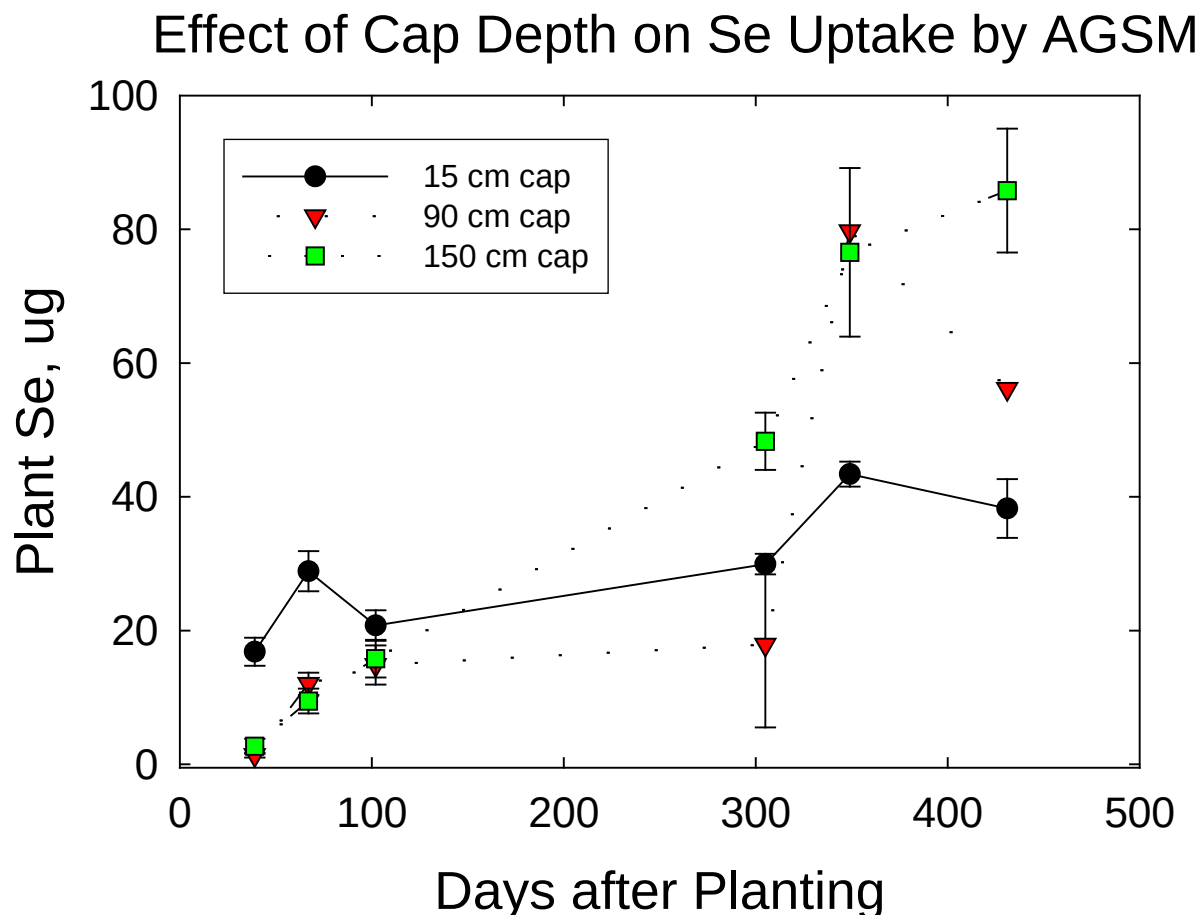


Fig. 10. Effect of cap depth over phosphatic shale (44.8 ± 8.9 mg/kg total Se) on mean $\pm$ standard error amounts (concentration $\times$ biomass) of Se in AGSM at six cuttings. 15-cm cap = 15 cm of topsoil, 90-cm cap = 30 cm of topsoil + 30 cm of chert + 30 cm of limestone, 150-cm cap = 30 cm topsoil + 60 cm of chert + 60 cm of limestone. Phosphatic shale depth = 52 cm.

Water content at 15- and 45-cm depths in the 75-cm columns (15-cm soil cap over 52 cm of phosphatic shale) responded rapidly to water additions (Fig. 11). Water content increased rapidly from air-dry (< 0.1 cm³/cm³) to saturation after the initial water addition (1st blue point on the left of each top, middle, and bottom figure). Thereafter, water content remained approximately constant during the initial growth period and then increased and decreased in response to evapotranspiration and water additions. These water content changes had no effect on plant Se concentrations in the 75-cm columns (Fig. 8) and also had little if any effect on plant biomass (Fig. 7).

Water content at the 30-cm depth in the 150-cm columns (30-cm soil + 30-cm chert + 30-cm limestone cap over 52 cm of phosphatic shale) also responded rapidly to water additions (Fig. 12). However, water content at 60-, 90-, and 120-cm depths showed little response to water additions after the initial column saturation and generally decreased during the fall of the first growing season in response to evapotranspiration and a gradual decrease in the frequency of water additions. The initial saturation of the

column material and subsequent drying of the columns mimics field conditions in which waste rock dumps tend to be at or near saturation during and after snowmelt and then dry out during the summer and fall as precipitation levels tend to decrease during the summer and into fall.

With increased water additions and reduced evapotranspiration in the winter and spring of the 2nd growing season, water contents at the different depths in the 150-cm columns were restored to their original levels and thereafter responded to evapotranspiration as plant growth increased with increasing daylength and to water additions. Column 6 water contents had the greatest response to water additions and evapotranspiration. Poor plant growth in columns 4 and 5 during the 2nd growing season may have been a response to overwatering. Because of the decrease in biomass production in these two columns, evapotranspiration decreased and water contents at the 60, 90, and 120-cm depths tended to remain constant through the 2nd growing season.

As with the 150-cm columns, water content at the 30-cm depth in the 210-cm columns (30-cm soil + 60-cm chert + 60-cm limestone cap over 52 cm of phosphatic shale) also responded rapidly to water additions (Fig. 13). However, water content at deeper depths showed little response to water additions after the initial column saturation and generally decreased during the fall of the first growing season in response to evapotranspiration and a gradual decrease in the frequency of water additions. The low water content in the middle of the chert layer (60-cm depth) during the fall part of the growing season indicated that the chert layer with its large coarse fragment content was acting as a partial capillary break. However, this was not sufficient to prevent Se uptake by some AGSM roots reaching the shale layer since Se concentrations in AGSM in the 210-cm columns with the 150-cm cap reached the same level as those in the 75-cm columns with the 15-cm soil cap by the 3rd cutting at the end of the 1st growing season (Fig. 8). Thus, root interception can to some extent negate the benefit of waste shale caps.

Because of increased water additions and decreased evapotranspiration in the winter and spring of the 2nd growing season, water contents at the different depths in the 210-cm columns were restored to their initial levels. Thereafter, water contents responded to water additions and evapotranspiration with the largest changes occurring at the shallower depths (30 and 60 cm). Water contents at the 90, 120, 150, and 180-cm depths in columns 7 and 8 tended to decline as the 2nd growing season progressed, but remained relatively constant in column 9.

Despite the large changes in water content at various depths in the columns, Se concentrations in AGSM topgrowth varied little over two growing seasons (Fig. 8) suggesting that the normal seasonal rise and fall in soil water content has little effect on plant uptake of Se. Prolonged saturation or drying may be necessary to alter soil conditions sufficiently to affect Se uptake, either by altering availability of soil Se or by influencing Se uptake physiology within the plant.

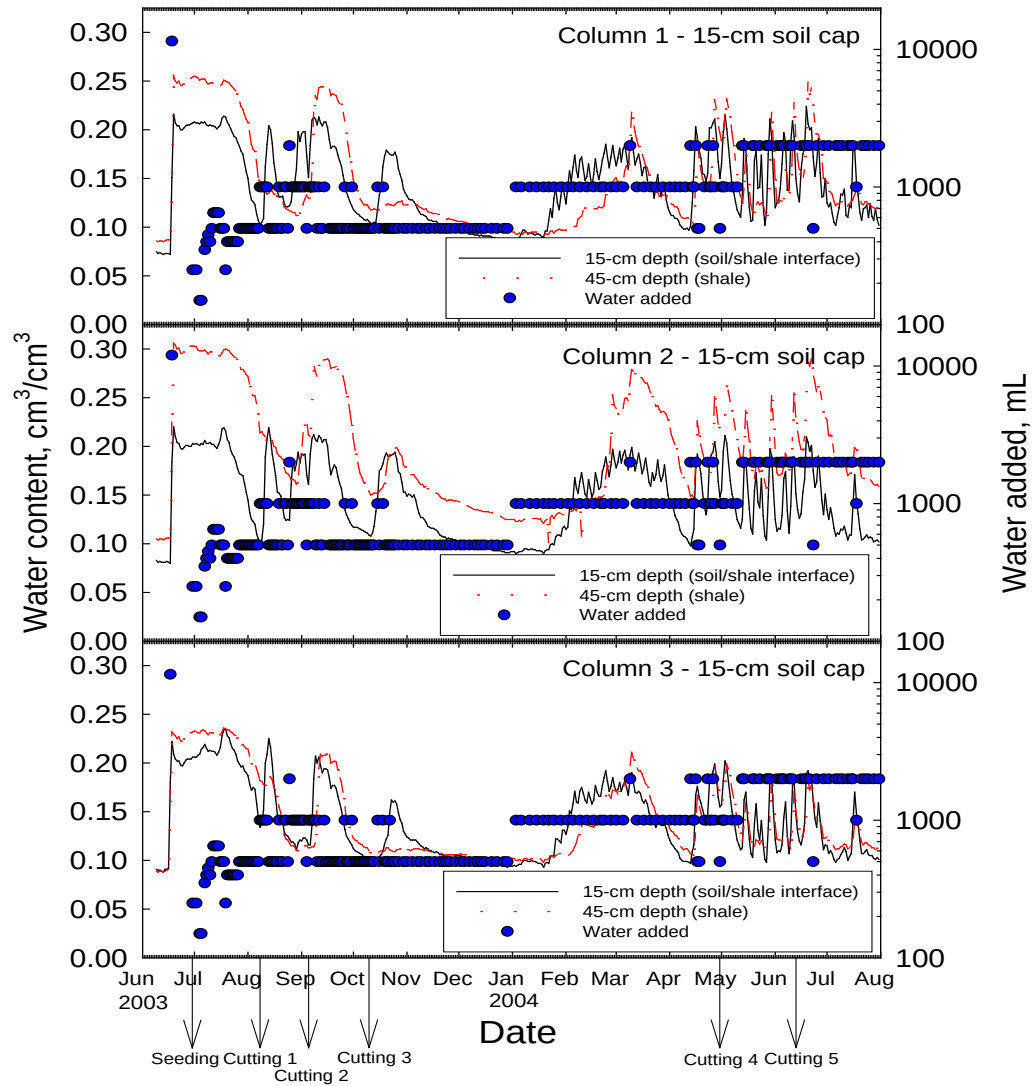


Fig. 11. Water added and volumetric water content of columns with a 15-cm soil cap over 52 cm of phosphatic shale.

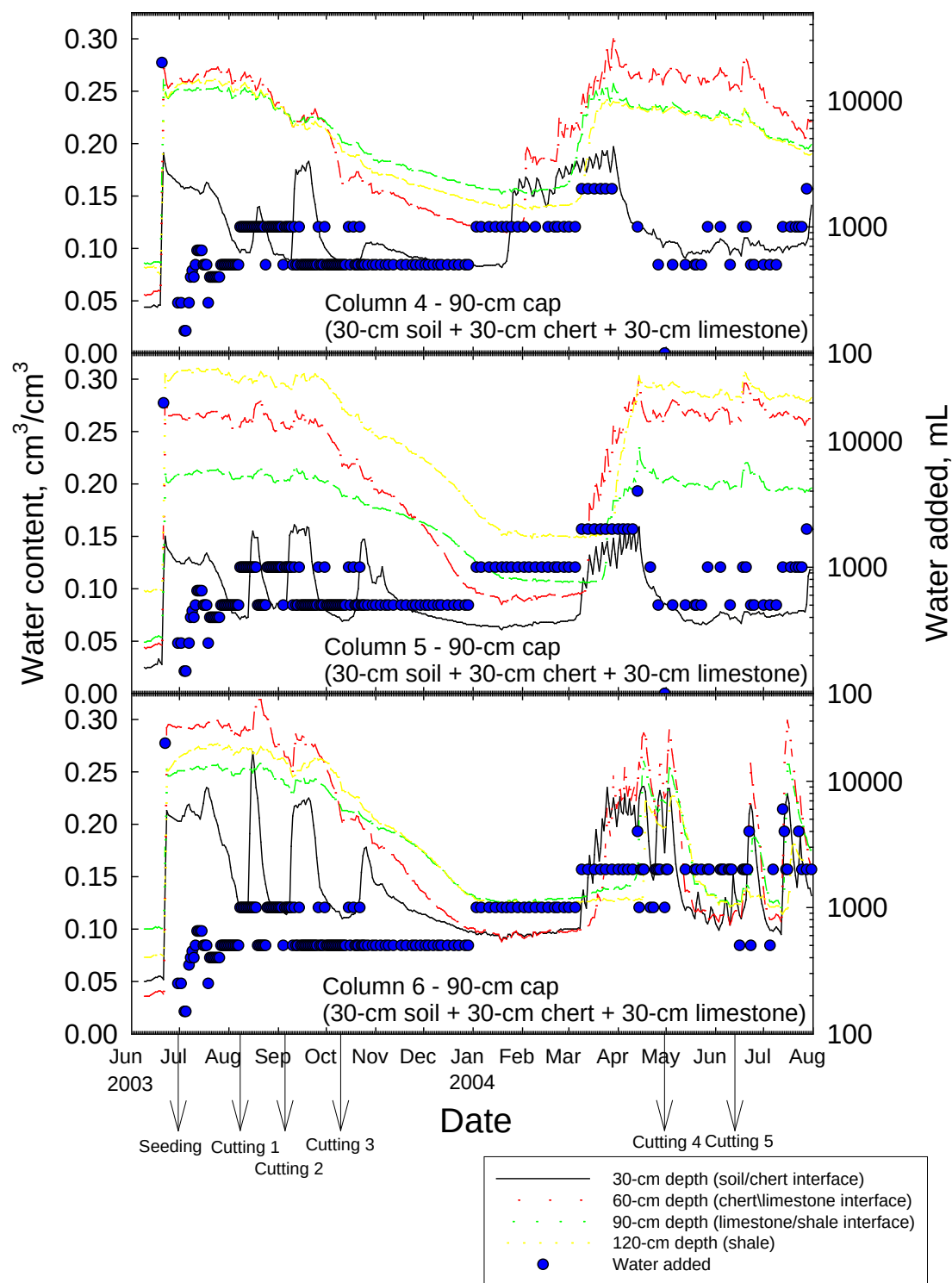


Fig. 12. Water added and volumetric water content of columns with a 90-cm cap (30-cm soil + 30-cm chert + 30-cm limestone) over 52 cm of phosphatic shale.

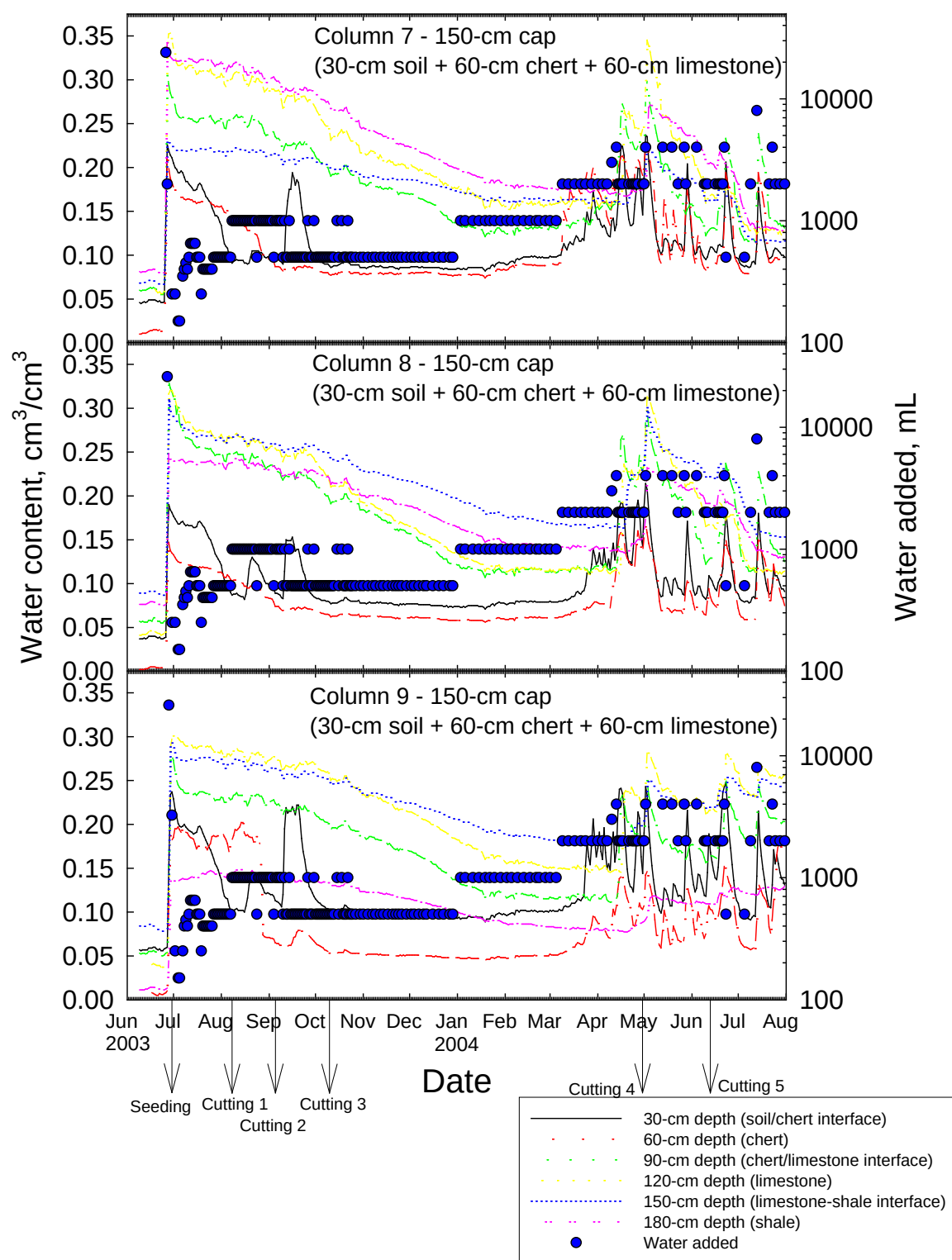


Fig. 13. Water added and volumetric water content of columns with a 150-cm cap (30-cm soil + 60-cm chert + 60-cm limestone) over 52 cm of phosphatic shale.

The thicker caps (90 and 150 cm) were unable to prevent uptake of Se by AGSM from the underlying phosphatic shale. The combination of root interception, capillary rise, and hydraulic lift will always result in some Se uptake by plants growing in caps over seleniferous phosphatic shale unless a complete capillary break or an exceptionally thick cap is used. This problem will tend to be more acute during mid to late growing season when plant roots are growing deeper to find water and evapotranspiration exceeds precipitation. However, prevention of Se uptake is not necessary to make effective use of capping materials such as soil, chert, and limestone. The only requirement is that Se concentrations be kept below 5 mg/kg to avoid potential toxicity to grazing animals. Even a very shallow cap (15 cm of topsoil) over a moderately-seleniferous waste shale (45 mg/kg total Se) will keep above-ground plant Se levels well below 5 mg/kg (Fig. 8) provided grass species are used where the majority of the rooting volume remains within the waste rock cap. Many areas of waste rock dumps contain total Se levels at or below this level and could be covered with a shallow cap and planted with native bunch grasses. Deep-rooted legume species such as alfalfa should be avoided because they tend to take up more Se than grasses (Mackowiak et al. 2004). Deep-rooted species will pull Se from deep in the waste rock dump to the above-ground portion of the plant, where the Se will continue to be cycled at the soil surface as plant tops decay, release Se that is free to leach through the rooting zone, and be taken up again the plants.

Analysis of risk potential of increased Se uptake from chert and limestone caps based on the USGS database of Se levels in chert and limestone:

Hein et al. (2004) analyzed numerous rock samples from cherty shale, Rex chert, Rex chert – Meade Peak transition, and Meade Peak phosphatic shale members of the Phosphoria Formation at several exposed sedimentary rock units in southeast ID. We stratified their data by lithology and location (section) and plotted the data as box plots so that the range of Se values for each type of rock unit could be evaluated (Fig. 14). Using our recommended Se limits for chert and limestone from this report and phosphatic shale from a previous report (Mackowiak and Amacher 2005), it's clear that all of the cherty shale and Rex chert members they sampled would be safe to use as re-vegetated capping materials over seleniferous waste shale. Only the siliceous siltstone from the Rex chert – Meade Peak transition zone contained Se levels above all the recommended limits for the different types of materials. Phosphatic shale (box plot on right side) is not recommended as a planting medium unless the total Se level is below 1 mg/kg (Mackowiak and Amacher 2005). The sedimentary rock unit Se data from Hein et al. (2004) indicates that Rex chert – Meade Peak transition rocks should probably be regarded as seleniferous in the absence of total analysis data and should not be used as a waste rock dump capping material.

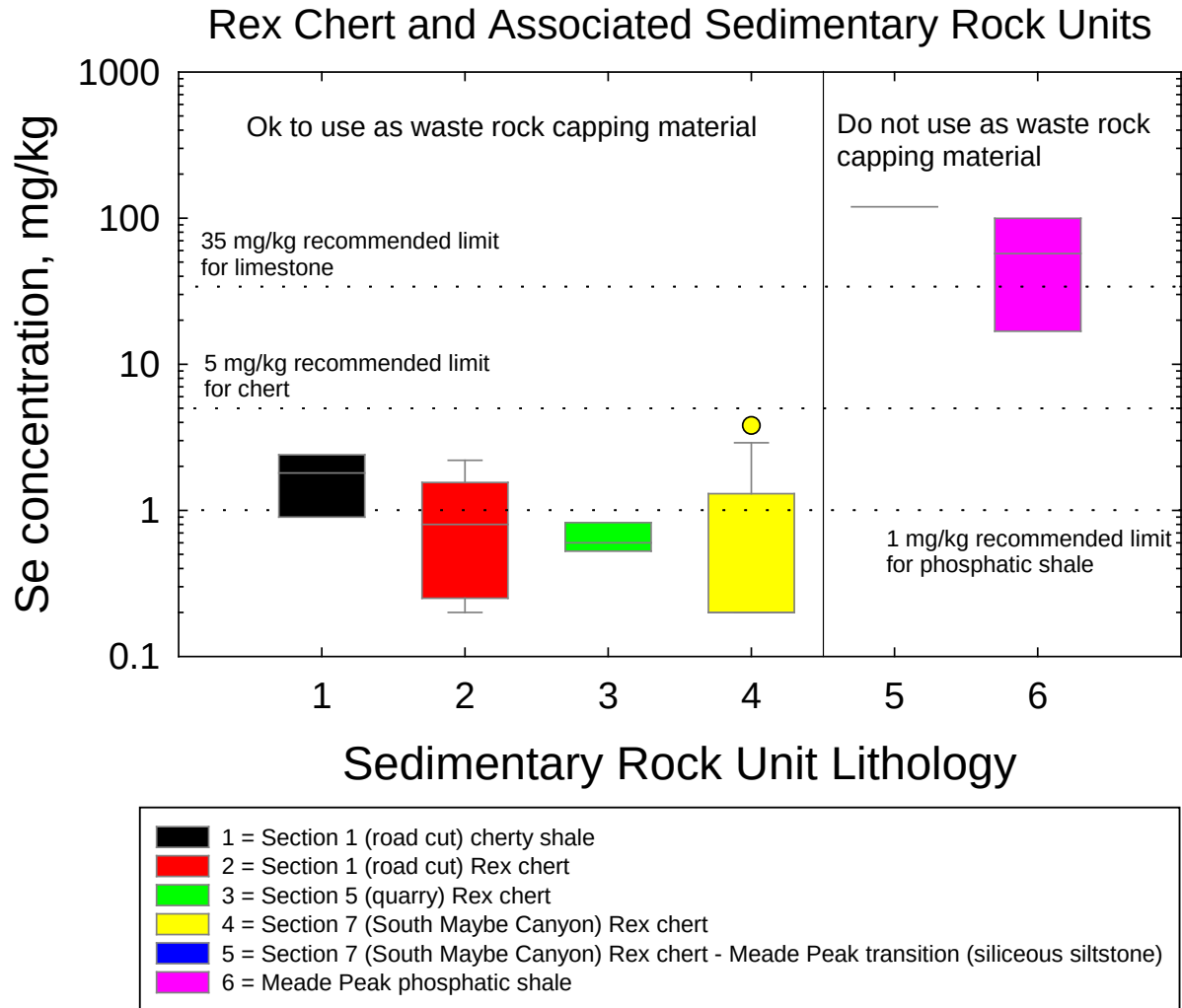


Fig. 14. Box plots of Se concentrations in cherty shale, Rex chert, Rex chert – Meade Peak transition, and Meade Peak phosphatic shale members of the Phosphoria Formation (data from Hein et al. 2004).

Herring and Grauch (2004) compiled an extensive database of Se and other data from sedimentary rock unit samples collected at Rasmussen Ridge, Dry Valley, Sage Creek, and Enoch Valley. We stratified their data by lithology and plotted their Se data as box plots to show the range of Se values for type of sedimentary rock unit (Fig. 15). All the Rex chert samples in the Hein et al. (2004) database contained less than the 5 mg/kg recommended limit for chert known to be safe for keeping vegetation Se levels below 5 mg/kg. There were only three Rex chert samples in the Herring and Grauch database. Two of these contained less than 5 mg/kg total Se (1.0 and 4.6 mg/kg total Se), but the third sample contained 837 mg/kg total Se, which produced the large range in the box plot shown on the left side of Fig. 15. There were two chert samples from within the Meade Peak member of the Phosphoria Formation and these contained 1.0 and 1.9 mg/kg total Se.

All the Grandeur dolostone and limestone samples contained less than the 35 mg/kg recommended limit for total Se in limestone as a capping material (3rd box plot from the left in Fig. 15). There were numerous dolostone samples collected within the Meade Peak member and most of these contained less than 35 mg/kg total Se, but 11 of 51 (20 %) Meade Peak dolostone and limestone samples contained more than 35 mg/kg total Se. The volume of dolostone and limestone units within the Meade Peak is probably not as extensive that available from the Grandeur member of the Phosphoria Formation. Thus, there is probably little need to save dolostone and limestone units within the Meade Peak for use as capping material and run the risk of encountering some high Se material when extensive deposits of the Grandeur units are available for use as a capping material and thus far, all of these have been found safe to use as capping material.

The Meade Peak carbon seam, mudstone, siltstone, phosphatic shale, and phosphorite units all contained total Se levels above the 1 mg/kg recommended limit for phosphatic shale in contact with plant roots (Fig. 15). We have not tested all the lithologies within the Meade Peak for plant uptake of Se, but we assume that all these units contain sufficient levels of plant available Se to produce Se levels in vegetation above 5 mg/kg. This assumes similar degrees of Se availability to plants in units of similar mineralogy.

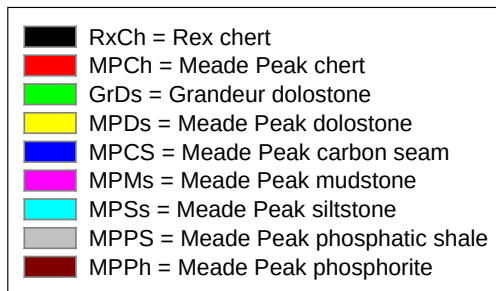
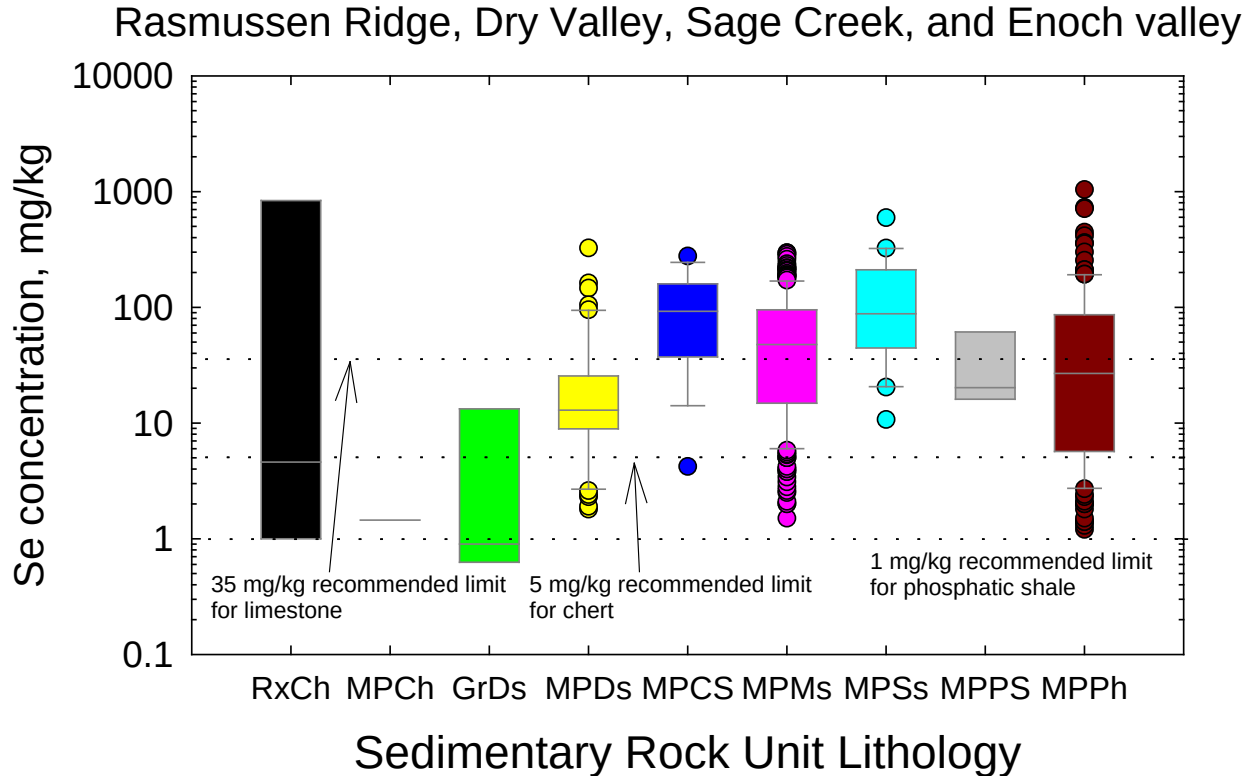


Fig. 15. Box plots of Se concentrations in Rex chert and various Meade Peak units of the Phosphoria Formation (data from Herring and Grauch 2004).

The possibility of finding Rex chert units with high levels of total Se led to a more extensive evaluation of Rex chert samples from Rasmussen Ridge and Enoch Valley (data provided by Herring and Grauch 2004). Dark-colored cherts tended to contain more total Se than light-colored cherts (Fig. 16) although there was some overlap. The dark-colored cherts had Se levels intermediate between the Meade Peak upper waste shales and the light-colored cherts. Chert color may be used as an approximate guide for stratifying chert samples by total Se levels, but it is not a substitute for total Se analysis. The database from Rasmussen Ridge and Enoch Valley also contained two Dinwoody Formation limestone samples and both of these contained low levels of Se (0.7 and 2.2 mg/kg total Se). Thus, Dinwoody limestone would also be a suitable capping material for waste rock dumps based on this analysis.

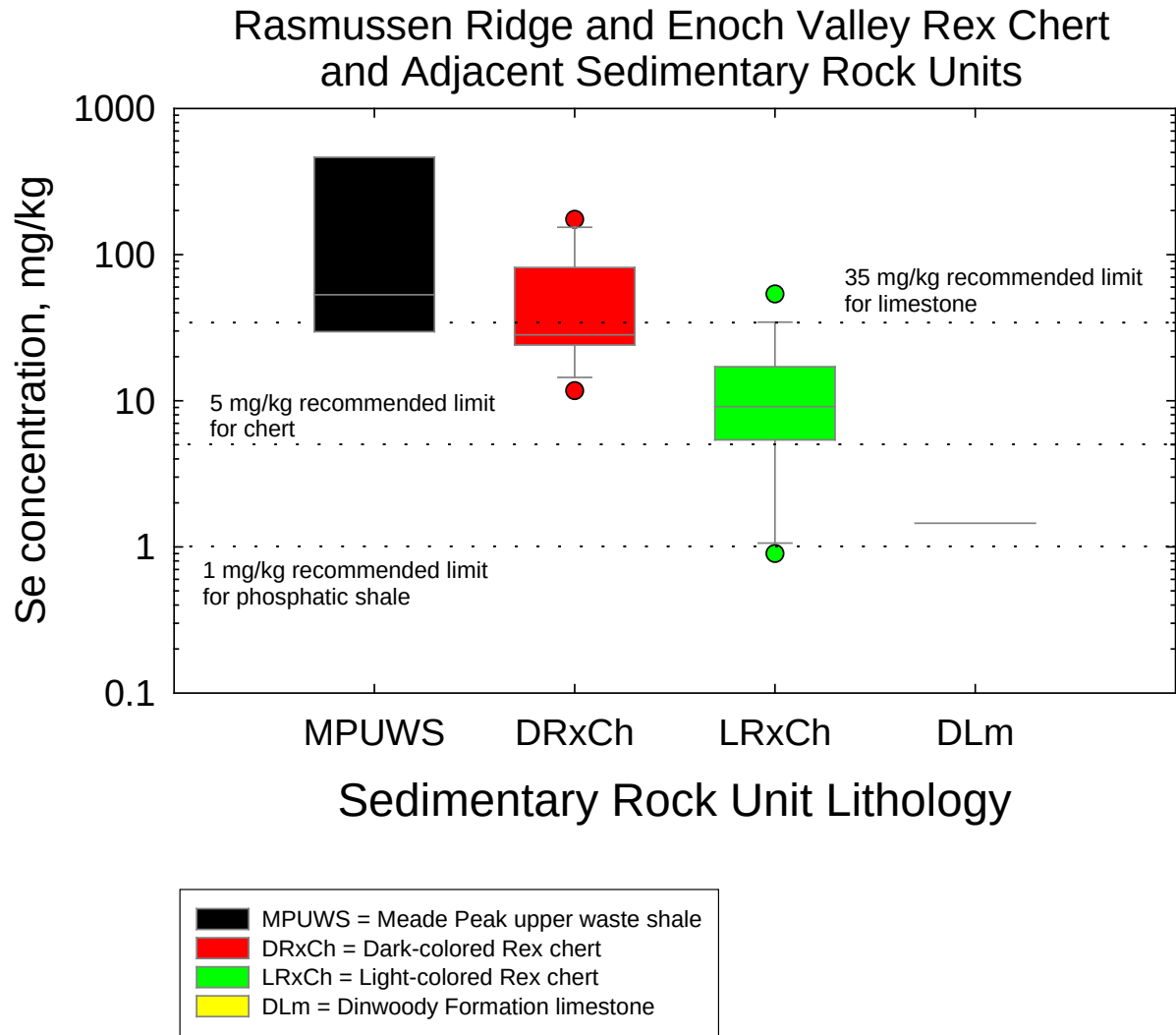


Fig. 16. Box plots of Se concentrations in Rasmussen Ridge and Enoch Valley Rex chert and adjacent sedimentary rock units (data provided by J.R. Herring, USGS, Denver, CO).

Recommendations:

Results of the glasshouse experiments and analysis of the USGS dataset lead to the following recommendations:

- Grandeur dolostone and limestone with Se levels below 35 mg/kg can be used safely as waste rock dump caps over waste shale for plant community establishment. There is little risk of increased Se uptake from these units. All the Grandeur dolostone and limestone samples in the USGS database contained Se levels below this recommended limit. However, 20 % of dolostone and limestone samples within the Meade Peak member contained more than 35 mg/kg total Se, suggesting that there is little likelihood of encountering high Se limestone or dolostone in the Phosphoria Formation except within the Meade Peak member. Thus, dolostone and limestone capping materials should be taken from the Grandeur member of the Phosphoria Formation and not from the Meade Peak.
- Rex chert with Se levels below 5 mg/kg can be used safely as waste rock dump caps for plant community establishment. Chert with higher Se levels might also have little increased risk of Se uptake, but should be tested in plant uptake experiments prior to use as a waste rock cap. Dark-colored cherts and cherts immediately adjacent to phosphatic shales or are part of the Meade Peak member should be avoided unless cleared by plant uptake experiments. As with soils, high Se cherts can be blended with low Se cherts to produce a capping material with less risk of increasing vegetation Se levels.
- Oxalate extractions show great promise for classifying sedimentary rock units on the basis of plant uptake of Se and should be used to test potential capping materials for Se bioavailability.

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